

(19) World Intellectual Property Organization
International Bureau



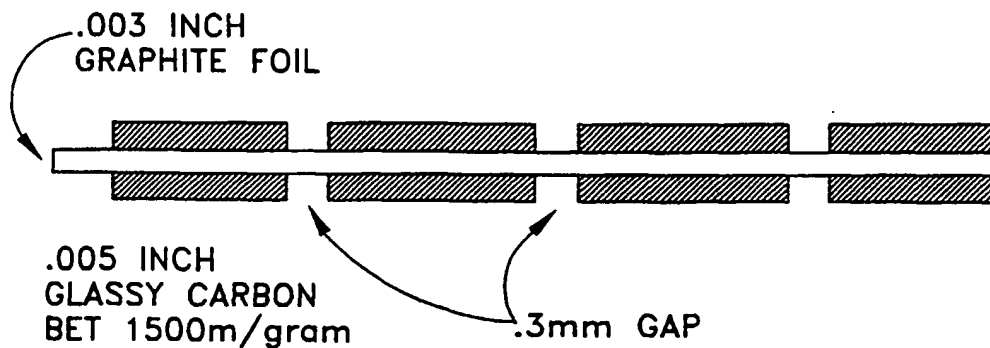
(43) International Publication Date
13 September 2001 (13.09.2001)

PCT

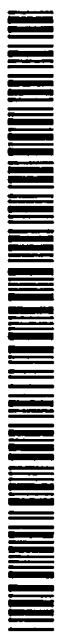
(10) International Publication Number
WO 01/66217 A1

- (51) International Patent Classification⁷: B01D 15/08 (81) Designated States (*national*): CN, JP, US.
- (21) International Application Number: PCT/US01/07295 (84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).
- (22) International Filing Date: 5 March 2001 (05.03.2001)
- (25) Filing Language: English Published: — with international search report
- (26) Publication Language: English
- (30) Priority Data: 06/187,351 6 March 2000 (06.03.2000) US
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
- (71) Applicant and
(72) Inventor: ANDELMAN, Marc, D. [US/US]; One Parkton Avenue, Worcester, MA 01605 (US).

(54) Title: LOW PORE VOLUME ELECTRODES WITH FLOW-THROUGH CAPACITOR AND ENERGY STORAGE USE AND METHOD



(57) Abstract: This invention relates to a low pore volume electrode wherein less than 50 % of its pores volume comprises macropores, and wherein a capacitance containing active layer is bonded to an integral current collector. The low pore volume electrode material acts as the active layer and may be comprised of a low pore volume carbon material. The integral current collector may be comprised of graphite foil and should be between 0.0001 and 0.1 inches thick. This low pore volume electrode may be used in a



VO 01/66217 A1

**LOW PORE VOLUME ELECTRODES WITH FLOW-THROUGH
CAPACITOR AND ENERGY STORAGE USE AND METHOD**

Reference to Prior Application

This application is based on and claims priority from
5 U.S. Provisional Patent Application Serial No. 60/187,351,
filed March 6, 2000, and is hereby incorporated by reference.

Background of the Invention

Surface area materials, especially those containing
carbon, between 30 meters per gram Brunauer Emmett Teller
10 method (BET) up to 3000 meters per gram or more BET, are
commonly used for double layer capacitors. Carbons may take
the form of fibers, powders, aerogels, or nanotubes. Pore
volume comes associated with the surface area necessary for
high capacitance, high performance electrodes. This pore
15 volume gets larger directly proportional to the amount of
macro versus meso and micropores. Lowering the surface area
lowers the pore volume, but, for a given material, also lowers
capacitance. Between electrode materials, selecting for a
preponderance of micro and meso versus macropores allows for
20 more useful surface area. Therefore, due to better surface
area utilization, even though surface area is lowered,
capacitance is still high. Since less surface area is required
for a given capacitance, pore volume is also decreased for a
given capacitance.

25 Pore volume is deleterious and especially bad for use in
a flow-through capacitor, but also for an energy storage
capacitor. During the regeneration or desorption cycle, salts
remain trapped in the pores and are not released from the pore
volume into the space between the electrodes. During the
30 subsequent purification or absorption cycle, these pore
volume salts are repurified from the pores and thereby create
an inefficiency. This pore volume inefficiency sets an upper
limit on the solution concentration that it is possible to

bonded to an integral current collector for use in flow-through capacitors meant to purify concentrated solutions, nor for energy storage purpose capacitors.

Summary of the Invention

5 The invention relates to a low pore volume electrode, flow-through capacitor and energy storage use and method. Therefore, an electrode with a low pore volume, capacitance-containing active layer would be desirable for use in a flow-through capacitor. The capacitance-containing active layer is
10 the material layer which contains most of the capacitance. Preferably, this electrode should contain an integral current collector bonded to the active, high capacitance electrode layers. This current collector should preferably be matched to the materials used in the active, high capacitance, low
15 pore volume electrode layers, such as carbon-containing active layers and graphite foil current collectors. Such an electrode would also be useful in an energy storage capacitor. In order to achieve this, a low pore volume electrode material is desirable. Such a material may be any surface area
20 material. Typically, such a material will be between 100 square meters per gram and 3000 square meters per gram. These materials need to be selected for pore volumes that are 1 cc/gram or less, preferably, 0.8 cc/gram or less. In order for the electrode to have desirable low series resistance, the
25 low pore volume, high capacitance material may be bonded to an integral current collector or it should have an integral current collector bonded to it. The current collector should be thin, so as not to take up excessive space. Ideally, it should be between 0.0001 and 0.1 inches thick, preferably
30 0.001 to 0.03 inches thick.

The invention comprises a low pore volume electrode material wherein less than 50% of its pore volume comprises macropores, with a capacitance-containing active layer bonded

1993; 5,196,115, issued March 23, 1993; 5,200,068, issued April 6, 1993; 5,360,540, issued November 1, 1994; 5,415,768, issued May 16, 1995; 5,538,611, issued July 23, 1996; 5,547,581, issued August 20, 1996; 5,620,597, issued April 15, 5 1997; 5,748,437, issued May 5, 1998; 5,779,891, issued July 14, 1998; Japanese Patent Application No. 18004/1993, filed January 9, 1993; PCT International Application No. US92/11358, filed December 31, 1992; PCT International Application No. US95/01653, filed February 9, 1995; Japanese Patent 10 Application No. 521326/1995, filed February 9, 1995; PCT International Application No. US94/05364, filed May 12, 1994; and PCT International Application No. US96/16157, filed October 9, 1996; and Japanese Patent Application No. Toku-gan-hei 10-253706, all incorporated herein by reference.

15 In order to achieve fast flow rate, the capacitor made from low pore volume materials must have low series resistance, for example, 0.01 ohms or less. Highly conductive current collectors are used in the industry in order to provide a conductive backing to the high resistance, active 20 electrode layer materials. According to this invention, it is desirable that the active layer be low in pore volume, so as to be useful for efficient purification, flow-through capacitors. U.S. Patent No. 5,150,283 describes metal foil current collectors with activated carbon attached by binders. 25 Selecting these activated carbons for low pore volumes, e.g., below 1 cc/gram, and preferably, below 0.8 cc/gram, would suit the purposes of this invention. However, metal foils tend to corrode and also have a high Schottky barrier, which causes a contact resistance intrinsic to the dissimilar carbon and 30 metal materials. In U.S. Patent No. 5,620,597, issued April 15, 1997, Figs. 13A through 13D, and column 11, line 45 to column 12 line 3, describe a carbonaceous graphite foil current collector that is a better materials match with

between 0.2 and 200 mils. However, for thicknesses much over 0.4 mils, surface stresses tend to crack the glassy carbon coating. To alleviate these stresses and facilitate manufacturing, it is desirable to incorporate x-y or radial
5 grids of naked, bare electrode. This can be achieved by masking the graphite foil, applying the glassy carbon precursor on top of the mask, and pyrolyzing.

Alternatively, a low carbon-containing blocking agent, for example, wax or any other ablatable compound, may be
10 painted on the graphite foil in the desired grid pattern. The glassy carbon precursor is painted, doctor bladed, sprayed, or otherwise deposited on top, but does not adhere to the wax or blocking agent. The precursor, such as, but not limited to any of the glassy carbon precursors, may include phenolic
15 resin, furfural alcohol, mesophase pitch, polyimide, etc. Upon pyrolyzing, this blocking agent ablates away, thereby leaving a grid of naked graphite foil. As the thick layers of glassy carbon shrink during firing, the grid patterns can shrink along with the overall electrode, thereby relieving
20 stresses and preventing cracking during manufacture. The graphite foil layer should be between 2 mils and 50 mils, and preferably 3 to 13 mils.

Brief Description of the Drawings

Fig. 1A is a top plan view of a glassy carbon electrode;
25 **Fig. 1B** is a side view of the glassy carbon electrode of **Fig. 1A**; and

Fig. 2 is a schematic illustration composed of a nanolithic electrode of aligned nanotubes attached to a graphite foil.

Description of the Embodiments

30 **Figs. 1A and 1B** illustrate a glassy carbon electrode with embossed lines to prevent stress cracking during manufacture,

respect to diameter, length, material, or wall thickness. The nanotubes may be subsequently treated, e.g., thermally or chemically, as to enhance surface area, such as by acid treatment. One advantage of nanotubes is that the ionic
5 conductive path is relatively straight down through the nanotubes. This lessens the pore resistance that occurs in activated carbon and similar pore systems which present labyrinthine pathways for the ions to work through. The nanotubes may be preferentially attached more or less
10 perpendicular to the current collector. Aligned nanotubes, as may be grown in a tube furnace, require a substrate to support the nanotube catalyst. This is shown on the Web site http://bucky5.wustl.edu/Science/Nanofiber_Growth.html. However, no prior art teaches dual use of a substrate as both
15 a catalyst support and an electrode current collector. For the purpose of this invention, the catalyst supporting substrate/current collector may be any metal foil. A preferable embodiment is graphite foil, since this has a similar material composition to the nanotubes, and therefore,
20 offers a lower Schottky barrier.

The catalyst may be any metal, metal-containing compound, such as: iron; nickel molybdenum; etc., that is used to catalyze the growth of nanotubes. In order to ensure that the nanotubes are tightly adhered to the substrate, the catalyst
25 may be applied with a mixture of phenolic resin, mesophase pitch, furfural I alcohol, or other carbon-containing adhesive mixture. This mixture is pyrolyzed, either prior to or during nanotube formation, thereby firmly adhering catalyst microparticles, in a carbon or glassy carbon matrix, onto the
30 surface of the substrate material. Nanotubes formed from this adhered catalyst are better adhered to the integral current collector substrate material for optimum performance as a capacitor electrode, whether for a flow-through capacitor or

capacitor containing 10 anode/cathode pairs of four by four inch sheets, separated by a 0.01 inch thick open screen netting material spacer defining a flow path. The capacitor is incorporated in a PVC, box-shaped cartridge holder provided with an inlet and an outlet. An oily waste mixture containing suspended oil droplets in concentrated brine of 10,000 ppm salt is passed through the capacitor at 100 mls/minute and purified to a level of 1000 ppm salt in a batch recycle loop mode. This breaks the colloidal suspension, allowing the oil droplets to coalesce together and separate from the water. The oil is then skimmed off from the water and recovered.

Example 2

Graphite foil, 5 mils thick, is coated with a mixture of an adhesive hydrogel, such as: polyvinyl alcohol; polyvinyl pyrrolidone; gelatin; and a nanoparticulate metal catalyst, such as molybdenum nanoparticles of less than 20 nanometers in diameter. Alternatively, any nanoparticle colloid or nanoparticle-polyelectrolyte mixture may be applied to form a nanoparticle layer on the graphite foil. Upon heating in the nanotube forming oven, the low carbon-containing hydrogels or polyelectrolytes ablate away. Aligned carbon nanotubes are grown by disproportionation of CO₂ in a tube furnace at 1200°C. The resultant nanotubes are 5 nanometers in diameter and 10 microns tall, with a length to width ratio of 2000 and a BET surface area of the nanotube layer of over 800 square meters per gram, a capacitance of over 0.8 farads per square centimeter of electrode plane area surface, and over 80 farads per gram of the combined electrode current collector material. Pore volume is less than 0.004 cc per each farad capacitance, and inefficiency, due to repurification of pore volume ions, is less than 20% when these electrodes are built into flow-through capacitors, according to the designs in U.S. Patent

Example 5

Graphite foil, 3 mils thick, is painted with a mixture of phenolic resin and iron nitride, to form a catalyst-phenolic film layer. This is carbonized in a 1000°C oven to form a
5 0.0002 inch film of carbon with reduced metal nanoparticles less than 10 nm in diameter. Subsequently, the electrode formed by this process is a substrate on which to grow tightly adhered nanotubes for use as a capacitor electrode with an integral, graphite foil current collector.

10 Example 6

Carbon cloth with a pore volume of 0.8 grams/cc is used with a graphite foil current collector and a compression contact to build a flat plate, flow-through capacitor. This material is used to remove 90% of the ions from tap water for
15 a home water purification unit of 100 gallons per day, with an energy usage of 5 watt hours per gallon or less.

to above 1000 Brunauer Emmett Teller method (BET) to form a low pore volume, high capacitance coating of less than 1 cubic centimeter per gram (1 cc/gram) pore volume, greater than about 0.2 farads per electrode plane area square centimeter, 5 greater than about 20 farads per gram of electrode material, and greater than about 20 farads per cubic centimeter of electrode material, as measured in concentrated H₂SO₄.

Claim 11. The electrode of claim 1 wherein the high capacitance material comprises carbon powder.

10 **Claim 12.** The electrode of claim 1 wherein the current collector is compression, mechanically, or electrically bonded to the capacitance-containing active layer.

15 **Claim 13.** The electrode of claim 1 wherein the ionic conductive path into the pore system is relatively straight and less labyrinthine when compared to activated carbon.

Claim 14. The electrode of claim 1 wherein the high capacitance material has a pore volume of less than 0.8 cubic centimeters per gram (0.8 cc/gm).

20 **Claim 15.** The electrode of claim 1 which has 30 percent (30%) or more solids, and the solids have a density of about 0.7 grams per cubic centimeter (0.7 cc/gm) or greater.

Claim 16. The electrode of claim 9 with a stress relieving x-y grid embossed in the glassy carbon layer.

25 **Claim 17.** An electrode for flow-through capacitors or energy storage use satisfying all of the following requirements:

- a) a pore volume less than 1 cubic centimeter per gram; and
 - b) a surface area of between 30 and 3000 square meters per gram and greater than 30 percent of the pore volume representing pores with diameters less than about 50 nanometers.
- 30

Claim 29. The electrode of claim 17 with a pore volume of about less than 0.004 cubic centimeter per farad of capacitance.

Claim 30. The method of using the electrode of claim 1 in
5 a low electrical series resistance (ESR) capacitor of below about 0.1 ohms.

1/2

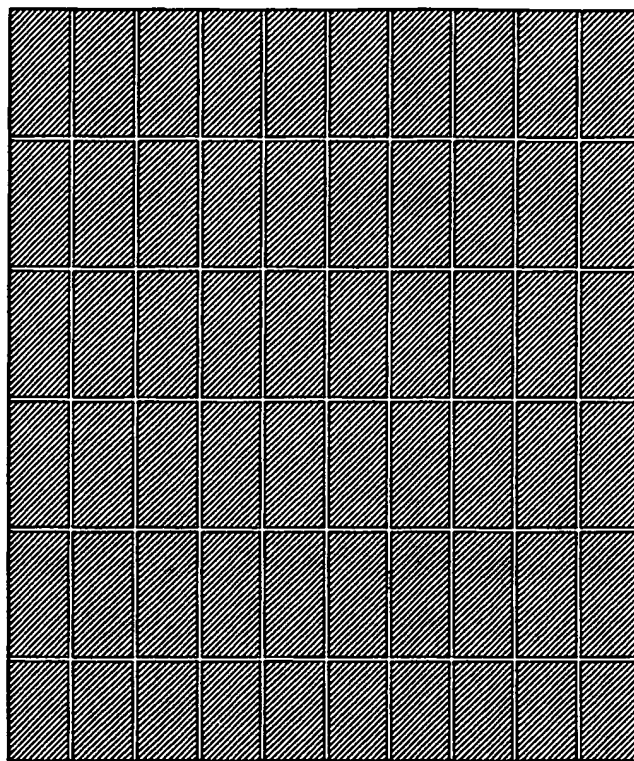


FIG. 1A

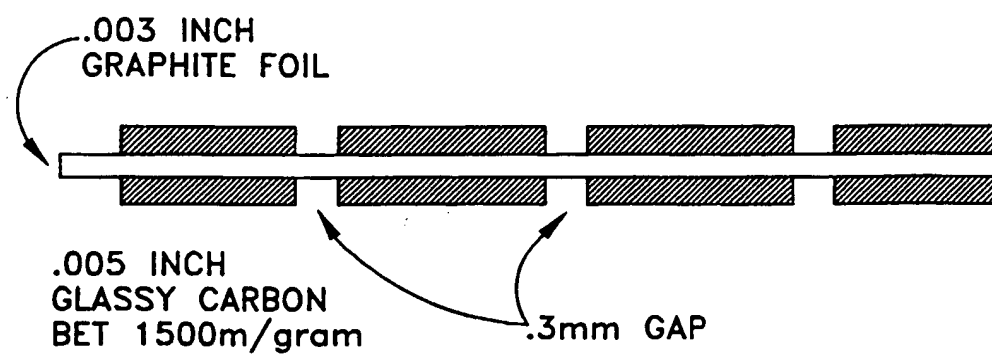


FIG. 1B

2/2

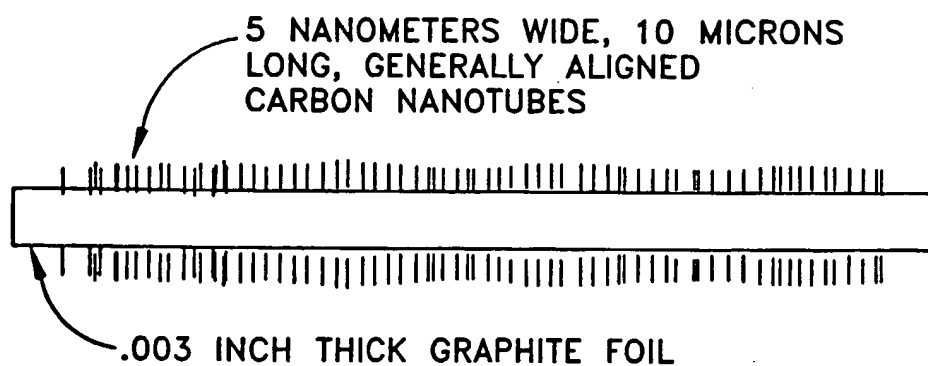


FIGURE 2, NANOTUBES DIRECTLY ADHERED
TO GRAPHITE FOIL TO FORM A CAPACITOR
ELECTRODE

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/07295

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01D 15/08

US CL : 210/198.2

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 210/198.2; 428/319.1; 204/665

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,192,432 A (ANDELMAN) 09 March 1993 (09.03.1993), claims 1, 3-5, 10.	1-2, 6, 10-13, 17-20, 23, 25, 27
X	US 5,476,734 A (PULLEY et al) 19 December 1995 (19.12.1995), column 1, lines 64-67; column 2, lines 1-25; column 3, lines 31-39; column 4, lines 15-25.	1-3, 5, 10, 12, 21, 30
X	US 5,620,597 A (ANDELMAN) 15 April 1997 (15.04.1997), column 4, lines 51-67; column 6, lines 1-15.	1-4, 6-30
X	US 5,538,611 A (OTOWA) 23 July 1996 (23.07.1996), column 1, lines 25-67; column 2, lines 1-46.	1-30

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

01 June 2001 (01.06.2001)

Date of mailing of the international search report

20 JUN 2001

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer

Leanna Roche

Telephone No. 703-308-6549